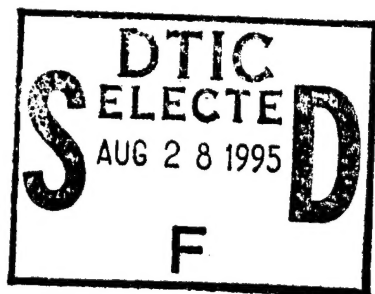OFFICE OF NAVAL RESEARCH

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Kenneth J. Wynne, Science Officer

FINAL REPORT

FIBER OPTIC RAMAN MEASUREMENTS OF
BONDING AGENTS AND INTERFACES
DURING THE CURING PROCESS

by

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13. ABSTRACT (Maximum 200 words) This project was aimed at understanding the curing of polymers using *in situ* fiber-optic Raman spectroscopy. In particular, the project emphasized curing at primarily glass interfaces, using chemometric analysis of Raman data obtained during curing.

• We have performed the first Raman study of the curing of a Polyimide using FT-Raman spectroscopy that employed statistical data determination and a comparison with DSC to demonstrate the ability of optical spectroscopic data to quantitatively determine the extent of curing.

• We have conducted *in situ* fiber-optic FT-Raman measurements of bulk polyimide polymers. Results from statistical analyses have been used to determine percent curing and stoichiometry in the polymers.

• Internal heat generation, transport and the effects of internal heat generation on reaction rates have been studied using fiber-optic methods.

• An *in situ* probe for fiber-optic Raman spectroscopy has been developed which is approximately the same size as a thermocouple, is inexpensive, easy to use and gives both temperature and cure information, with the percentage cure measurement having a standard error of 0.5% over the entire range of polymer curing.

• A polymer suspension of metal particles has been developed which is surface-enhanced Raman active, permitting the first optical study of the metal-polymer interface which has first-monolayer sensitivity in a bulk material.

14. SUBJECT TERMS

POLYMER, RAMAN, FIBER OPTIC, SPECTROSCOPY, EPOXY, POLYIMIDE, SURFACE, INTERFACE

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Brief Description:
  This project was aimed at understanding the curing of polymers using *in situ* fiber-optic Raman spectroscopy. In particular, the project emphasized curing at primarily glass interfaces, using chemometric analysis of Raman data obtained during curing.

Significant Results
- We have performed the first Raman study of the curing of a Polyimide using FT-Raman spectroscopy that employed statistical data determination and a comparison with DSC to demonstrate the ability of optical spectroscopic data to quantitatively determine the extent of curing.
- We have conducted *in situ* fiber-optic FT-Raman measurements of bulk polyimide polymers. Results from statistical analyses have been used to determine percent curing and stoichiometry in the polymers.
- Internal heat generation, transport and the effects of internal heat generation on reaction rates have been studied using fiber-optic methods.
- An *in situ* probe for fiber-optic Raman spectroscopy has been developed which is approximately the same size as a thermocouple, is inexpensive, easy to use and gives both temperature and cure information, with the percentage cure measurement having a standard error of 0.5% over the entire range of polymer curing.
- A polymer suspension of metal particles has been developed which is surface-enhanced Raman active, permitting the first optical study of the metal-polymer interface which has first-monolayer sensitivity in a bulk material.

FT-RAMAN OF A POLYIMIDE CURING REACTION

Polymer matrix materials like polyimides are frequently used in composites for the electronics and aerospace industries. Polyimides are resistant to high temperatures and have extreme stability and excellent mechanical and electrical properties. However, polyimide reactions are complex and are less well understood than those of other polymers.

Various optical spectroscopies have been applied to the curing of polymers, including UV-Visible absorbance, fluorescence,[1] near-infrared absorbance (NIRA)[2-4], mid-infrared (MIR) absorbance[5,6] and Raman[7,8].

UV-Visible absorbance is sensitive, but gives no direct information on chemical bonding. Absorbance peaks for the chromophores involved in bonding are broad and shift with temperature.

Fluorescence is very sensitive to changes in physical state. However, the quantum yield of fluorescence for a fluorophore depends on temperature, viscosity, curing, oxygen content, position near interfaces and other factors in a complex way. Direct chemical bond information is not obtainable from fluorescence.

NIRA gives direct bond information. However, absorbances in the IR-overtone region are weak and broad. NIRA is of limited usefulness if O-H bonds are present in the sample, because these vibrations have broad, intense overtone absorbances in the NIR.

MIR absorbance in the 2 to 15 μm wavelength range is recognized as an important laboratory tool for the analysis of chemical-bonding. However, for industrial work the MIR setup is incompatible with most commercial autoclaves. MIR also does not lend itself to remote measurement.[9]

Raman scattering is another powerful technique for chemical-bonding analysis. The availability of strong monochromatic laser sources and high quality detectors makes Raman spectroscopy practical. Raman is also more versatile than other techniques because it has an inherent ability to monitor the temperature of the sample it interrogates by comparing Stokes (lower energy) scattering and anti-Stokes (higher energy) scattering because the anti-Stokes scattering is highly temperature dependent. Previous Raman studies of interesting polyimides and precursors have included the band assignments for maleimide[10-12] and N-phenyl maleimide[13]. Raman after a partial cure (190°C, 2 hours) of methylene dianaline bismaleimide (MDA-BMI) was compared to an uncured sample and intensity changes were observed for four bands at 3104, 3094, 1585, and 1064 cm^{-1}. These bands correspond to the asymmetric and symmetric C-H stretches, maleimide C=C stretch, and in-plane C-H bend of the maleimide ring, respectively[13].

The Ciba-Geigy Matrimid 5292 system is derived from MDA-BMI. It is a two component system that consists of MDA-BMI (component A) and *O,O'* -Diallyl Bisphenol A (component B). In this report, we examine the Raman spectroscopy of the Matrimid cure system, assign some of the important cure-sensitive vibrations, and demonstrate that the Raman spectra are directly related to the extent of curing by comparison to differential scanning calorimetry. Principal component analysis (PCA) and regression analysis are used to develop predictive models for cure percent based on the FT-Raman spectra.

EXPERIMENTAL

Maleimide (99%) from Aldrich (Milwaukee, WI) and succinimide from Mallinckrodt (Chesterfield, MO) were used as supplied. Methylene dianaline bismaleimide and *O,O'* -Diallyl Bisphenol A are the two components of the Ciba-Geigy Matrimid 5292 system. We refer to these materials as component A and component B respectively. Both components were used as supplied. Formulation of the two component polymer was a 100:85 w/w mixture of components A and B, respectively. The resulting mixture was heated and stirred to 130°C and dispensed into one dram vials. The vials were placed in an oven equipped with a sand bath and cured isothermally. Six samples were simultaneously removed at intervals throughout the cure. The samples were cooled and refrigerated. FT-Raman spectra were acquired on a Perkin-Elmer 1700X NIR FT Raman spectrometer (Norwalk, CT). All samples were run at a wavenumber range of 3500 to 500 cm^{-1} for 16 scans at 4 cm^{-1} resolution and at 1 W of power. DSC thermograms were acquired on a Perkin-Elmer DSC 7 Differential Scanning Calorimeter (Norwalk, CT). All samples were run in standard aluminum pans at a temperature range of 50 °C-350 °C and at a scan rate of 10 °C/min. The last three groups of samples were considered "post cure" since no appreciable exotherm was obtained from DSC.

From each spectrum, thirty-one peaks of interest were selected. Their peak intensities were normalized to the internal standard at 1638 cm^{-1} (peak 10 in Figure 1).

Figure 1 - 31 peaks used for earliest PCA analysis of Polyimide Curing Reaction
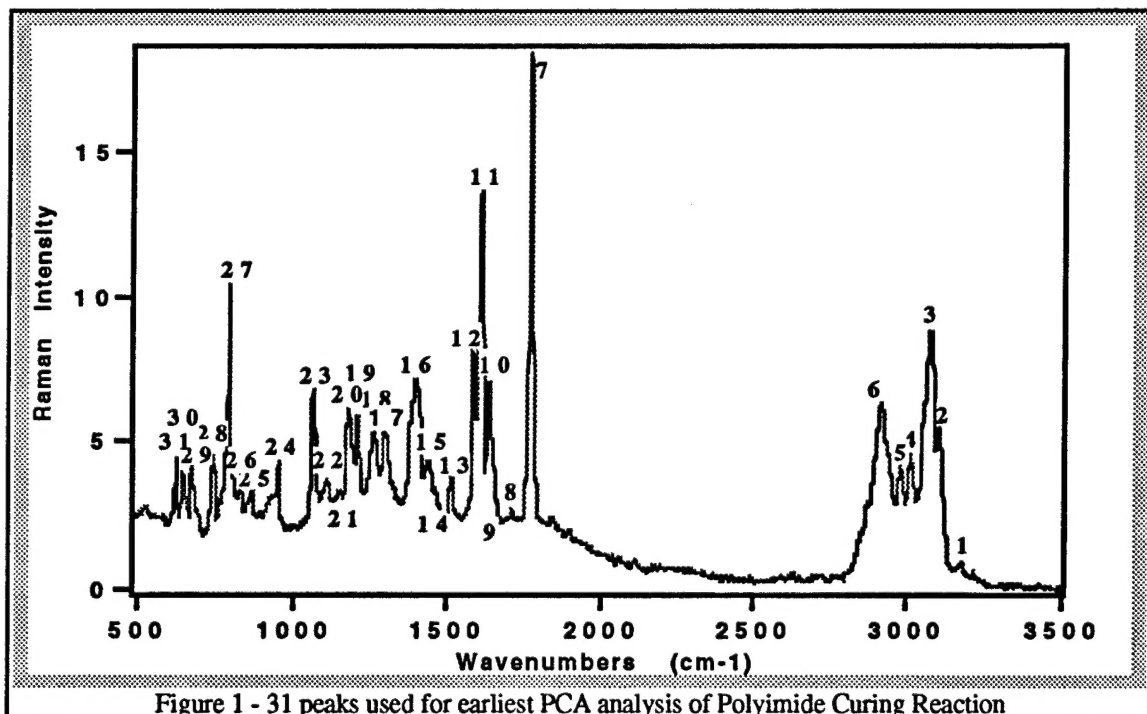
PCA was performed on this data set consisting of the normalized intensities of 31 peaks for each of 24 samples. Regression analysis was performed to correlate percent cure measured by DSC with the projections of the FT-Raman spectra onto the principal components. A MS DOS-based computer was employed for all computations. Data preprocessing and regression analyses were performed using Microsoft Excel 4.0. Principal component analysis was done using Systat version 4.0 (Evanston, IL).

Copolymerization of Components A and B. The main curing reaction mechanism was proposed to be a Michael-type addition. The resulting polymer would be linear and thermoplastic in nature and the maleimide alkene functionality will be eliminated[14]. The structures of components A and B along with the mechanism of the curing reaction are shown in Figure 2.

Figure 2 - Michael-addition mechanism for polyimide
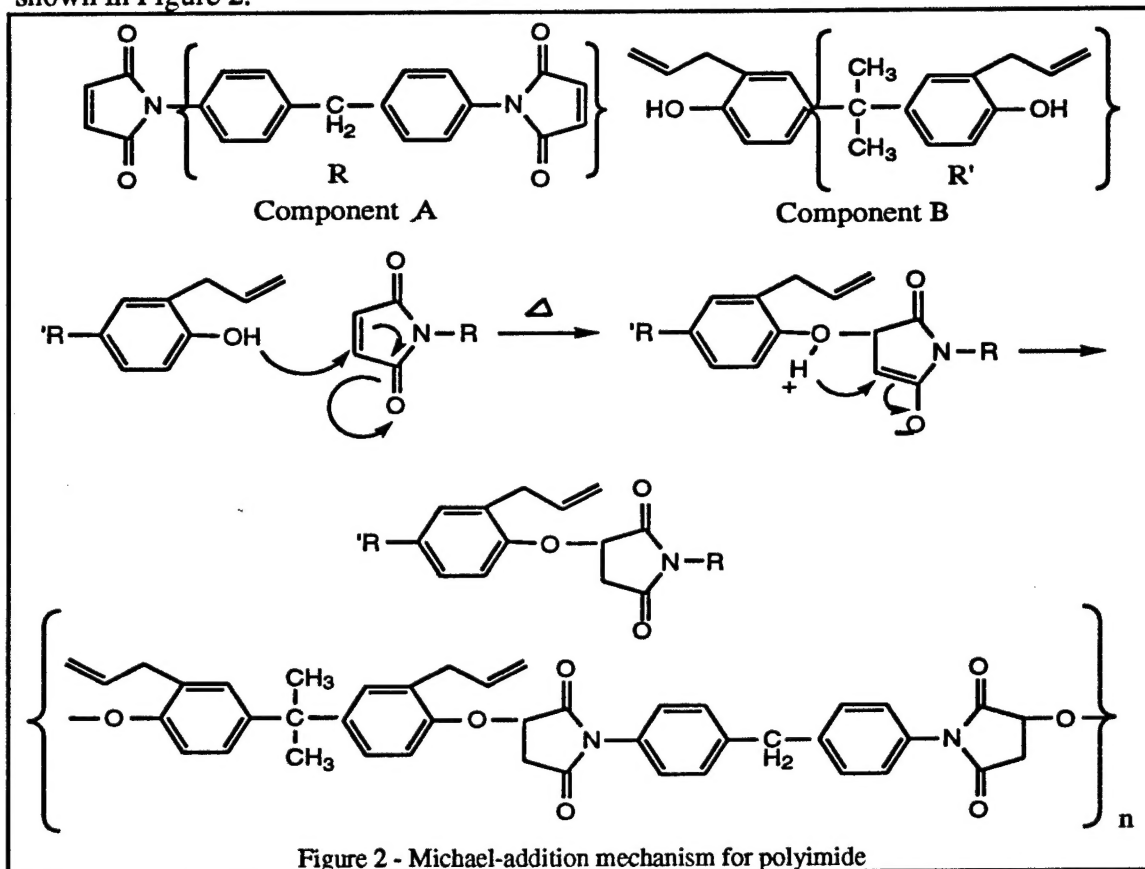
FT-Raman spectra of the separate components have been taken and are shown below in Figure 3.

Figure 3 - Spectra of components of Ciba-Geigy Matrimid Polyimide
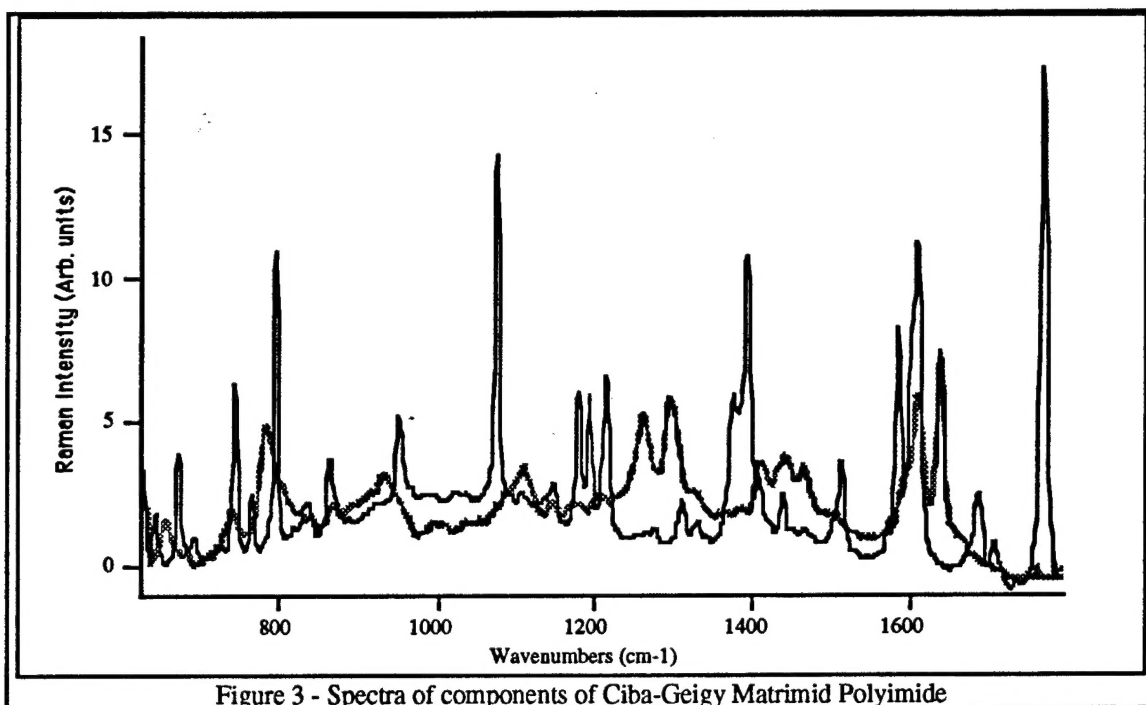
Multiple samples of partially-cured polyimide were removed from the curing oven/bath after the curing cycles in Table I.

TABLE I: Curing Cycles

FT-RAMAN LABELS	PCA LABELS	CURE TEMP. AND TIME
Control	A	no curing
Sample 1	B	180°C, 15 min.
Sample 2	C	180°C, 30 min.
Sample 3	D	180°C, 45 min.
Sample 4	E	180°C, 60 min.
Sample 5	F	180°C, 120 min.
Sample 6	POST CURE	180°C, 120 min.; 250°C, 120 min.
Sample 7		180°C, 120 min.; 250°C, 240 min.
Sample 8		180°C, 120 min.; 250°C, 360 min.

Figure 4 shows FT-Raman spectra of the control (no cure) and Sample 5 (76% cure).
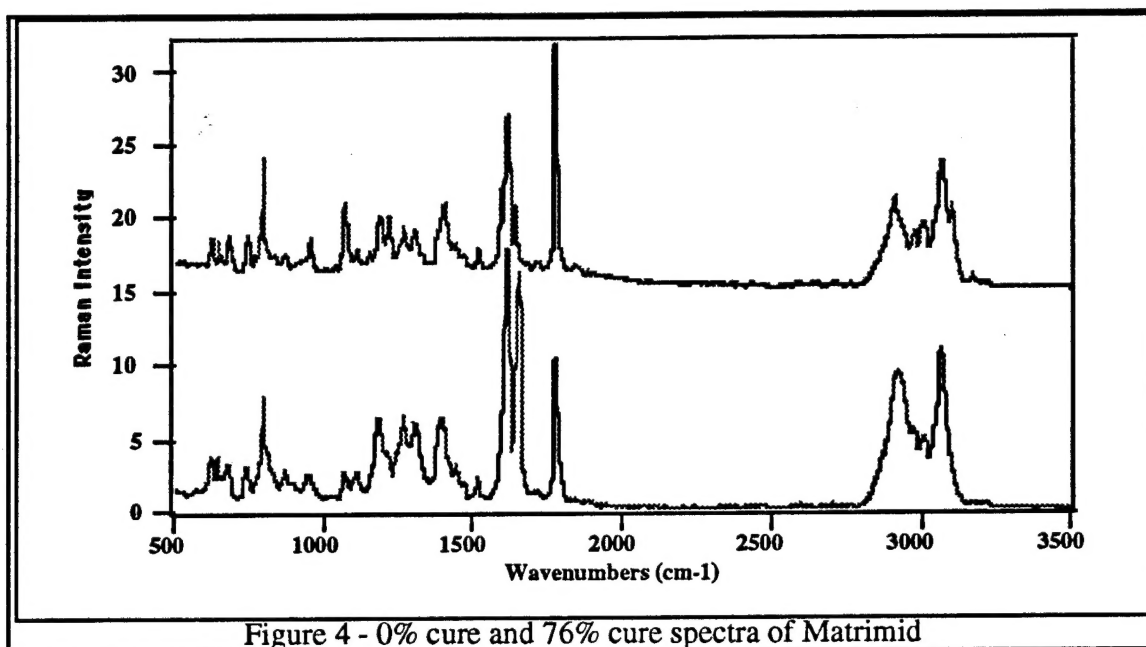
Figure 4 - 0% cure and 76% cure spectra of Matrimid

Table II lists major peak assignments obtained by comparison with model compounds, *ab initio* vibrational mode analysis and literature sources[10-13].
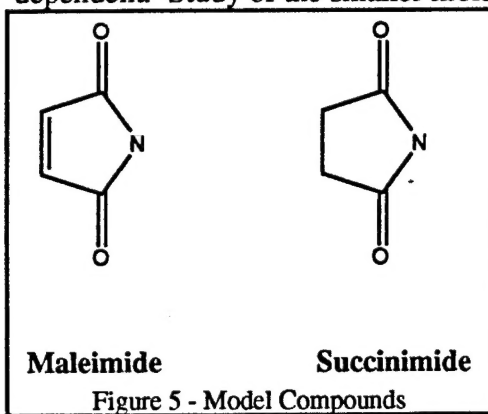
TABLE II: Major Peak Assignments

PCA PEAK NUM.	WAVENUMBER	ASSIGNMENT
3	3071 cm^{-1}	C-H stretch
6	2910 cm^{-1}	C-H stretch
7	1773 cm^{-1}	C=O stretch
10	1638 cm^{-1}	C=C stretch of comp. B
11	1610 cm^{-1}	C=C stretch of comp. B
12	1587 cm^{-1}	C=C stretch of maleimide
16	1398 cm^{-1}	C-N-C stretch
19	1210 cm^{-1}	N-Ph stretch
23	1065 cm^{-1}	mal. C-H in phase bend
27	793 cm^{-1}	symm ring stretch

The most obvious difference upon curing is the dramatic reduction of the peak at 1773 cm^{-1}, the C=O stretching frequency. We also observe the expected change in the C=C region. The control has a vibration at 1587 cm^{-1} assignable to the C=C maleimide stretch. Bands also occur at 1610 and 1638 cm^{-1}, C=C stretches of component B.

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Sample 5 has peaks at 1610, and 1638 cm^{-1}. These are the remaining C=C stretches of component B, and indicates complete loss of the maleimide alkene functionality, with a slight shift in the other peaks.
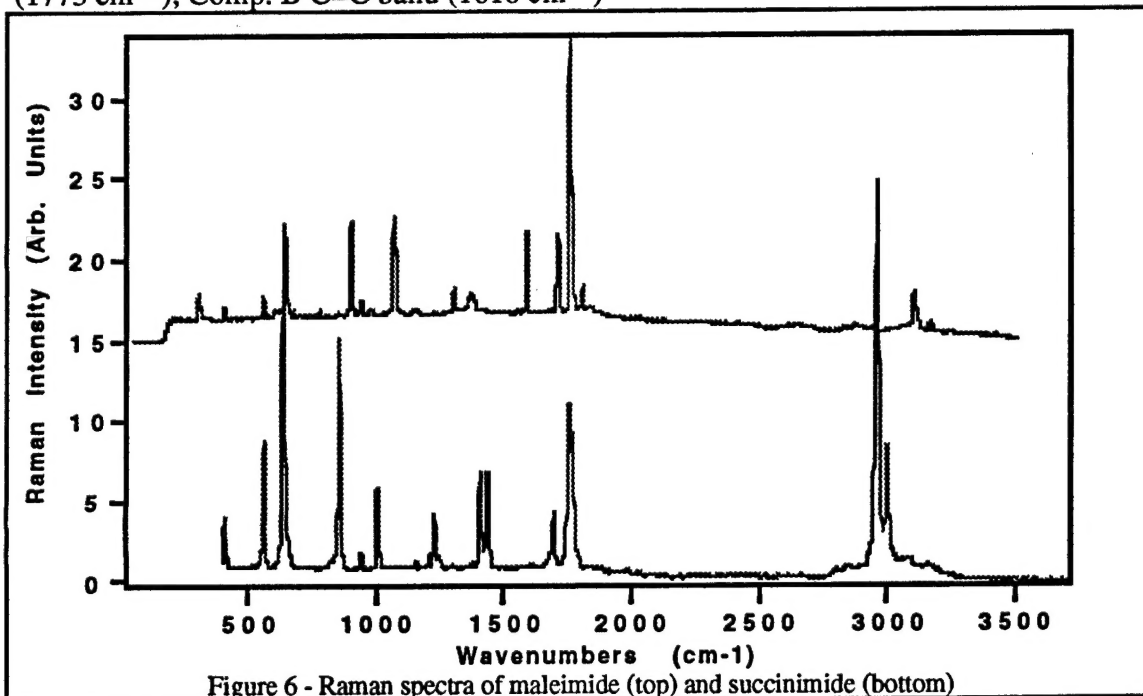
The reduction of intensity for the C=O peak at 1773 cm^{-1} is currently viewed as a unique marker of percent reaction of the polyimide alkene group because the C=O functionality is unaffected by curing, although its Raman cross-section is highly cure-dependent. Study of the smaller molecules maleimide and succinimide (Figure 5) reveals a direct relationship between the existence of a maleimide C=C bond (1587 cm^{-1}) and the C=O (1773 cm^{-1}) intensity (Figure 6). *Ab initio* calculations predict a similar relationship. We interpret this to mean that the breakage of the maleimide C=C bond disrupts the conjugated Π system of the maleimide, reducing polarizability and thus decreasing the Raman intensity of the C=O peak.

Using the conserved C=C peak of component B at 1638 cm^{-1} as an internal standard, peak intensity ratios were determined for the C=O band (1773 cm^{-1}), Comp. B C=C band (1610 cm^{-1})

Maleimide   **Succinimide**

Figure 5 - Model Compounds

Figure 6 - Raman spectra of maleimide (top) and succinimide (bottom)

and the maleimide C-H in phase bend band (1065 cm^{-1}). These particular bands were chosen because they undergo a significant reduction in their intensity during the curing process. These same samples were then studied with DSC to determine percent cure

An isothermal analysis was performed on the control to determine theoretical cure percentages as a function of time at a given temperature. These were then compared to cure percentages based on DSC analysis of the other samples. The results are shown in Figure 7. The DSC analyses of the oven samples generally follow the predicted curing
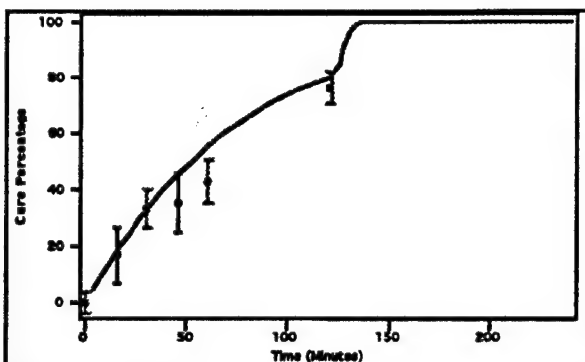
10

Figure 7 - observed vs. theoretical cure of Polyimide

curve within experimental error. Plots of peak ratios *versus* cure percentage show a relationship between relative peak height of the three cure-sensitive vibrations and extent of cure. This clearly shows that Raman spectra can be directly related to the extent of curing by comparison with DSC. During the curing process (Figure 1) the maleimide C=C functionality is lost. As a result, peaks in the Raman spectrum at 1065 cm^{-1} (the maleimide C-H bend) and 1587 cm^{-1} (the maleimide C=C stretch) decreases in intensity with curing and become negligible compared to the reference peak. The peak at 1773 cm^{-1} (the maleimide C=O stretch) decreases with relative intensity versus the reference, but does not disappear.

Any of these single peaks could be used to predict percent cure from Raman spectra. However, a more inclusive approach using pattern recognition techniques is more useful. As an example, the cure data were re-evaluated using principal component analysis (PCA).

Principal Component Analysis. Each spectrum can be mathematically treated as a data point (or vector) in a measurement space of wavelengths (or variables). Although the intensities for a large number of variables are measured, the spectral intensities are not independent of one another. The spectral intensities of adjacent wavelengths tend to be highly correlated; additionally, the intensities at certain other wavelengths may rise and fall together as a consequence of correlation with chemical structures present. This colinearity means that the data matrix will have dominating directions of variability that will contain most of the information in the data set. Thus, the inherent dimensionality of the data is always much lower than the number of variables.

Accounting for the variability in a data set requires a number of principal components (PCs) equal to the smaller of the number of variables or the number of samples[15-17]. The first PC (PC1) is the line that best fits the data variability, with the sum of squares of deviations of the data points from this linear combination of the original axes a minimum. The second (PC2) and higher PCs are perpendicular to this axis and are ranked in decreasing order of correlation with the data. This decomposition of the data matrix can be obtained by eigenvalue-eigenvector analysis. The resulting eigenvalues measure the variance explained by each PC. As the amount of explained variability decreases for each added PC, a cutoff point may be decided after which the remaining PCs are considered to consist mostly of uncertainty. PCA thus re-expresses the variability present in the higher dimensional space into a space of fewer dimensions. A plot of the data projected on the plane of the first two or three PC's may permit relationships or trends among the clusters of data points to be visualized in two or three dimensions. Once the information in a data matrix is compressed to its most relevant features by PCA, the data points (spectra) projected into the principal component space can be regressed on (fitted to) chemical properties of interest for calibration purposes. This technique is termed principal component regression (PCR)[18,19].

The trend in the FT-Raman data revealed by PCA follows the chemical changes occurring during the curing process. The first three principal components of the Raman spectra data set accounted for 99.2% of the variance in the data: 96.3% by PC1, 2.3% by PC2 and 0.6% by PC3. The projections of these spectra onto the first three principal components show a trend of the spectra from 0% cure (A) to 76% cure (F). When PCR is performed on the percent cure against the projections onto the first principal component, a nearly linear fit is obtained with an R^2 of 0.83.

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Post-cure. PCA and other analyses indicate that the full curing reaction is not a simple linear process. Figure 8 below shows the "Scores Plot" of a set of curing spectra on the first two principal components. These results indicate that a minimum of two major reactions occur during the curing process; these occur at different times and temperatures. At the end of the cure, a third process is observed: a distinct post-cure reaction. The projections for samples having the highest percent cure (76%) are somewhat removed from the cluster of lower cure values, and some curvature in the data may be seen. The later curing reaction and post-cure seem to be marked by cross-linking reactions that consume some of the C=C functionalities of component B. An in-depth investigation of this latter mechanism is currently in progress.
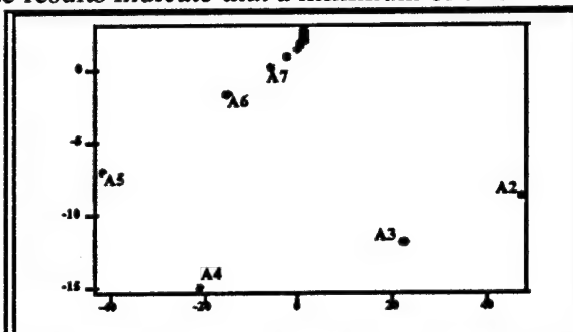

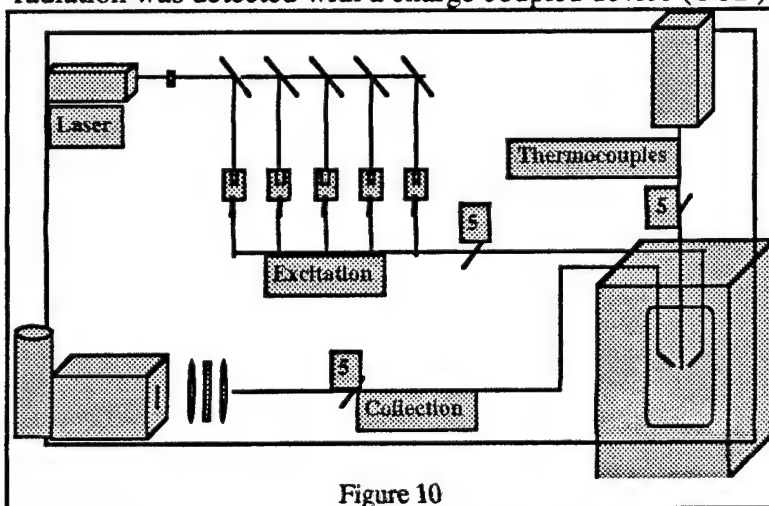Figure 8 - Scores Plot of Raman Spectra on First Two Principal Components

"Homopolymerization" of Component A. We repeated the MDA-BMI homopolymerization experiments reported in Ref. [13] and confirm the changes reported. There were slight changes in the four bands: 3104 and 3094 cm^{-1}, C-H stretches; 1585 cm^{-1}, maleimide C=C stretch; and 1064 cm^{-1}, maleimide C-H in phase bend. However, these changes were observed after only 30 min. at 180°C, much earlier than reported. These changes mimic those observed during the cure of components A & B together. However, the dramatic C=O peak (1773 cm^{-1}) intensity reduction which indicates the maleimide C=C bond breakage does not appear in their data for the homopolymerization of component A. We conclude that the alkene groups in component A are not lost during the initial "reaction". Reduction in the C=O stretching intensity after 1520 min. indicates that homopolymerization of component A does occur, but is very slow. DSC data for component A indicate that the reported spectral changes are associated with melting of microcrystallites. Upon cooling, component A appears to form a glass of supercooled liquid, with no apparent phase change in the broad melting range observed on a first scan.

Laboratory Measurements of Curing

The curing of a DER332-Jeffamine T-403 epoxy system has been studied using FT-Raman spectroscopy, Argon-ion-laser-excited Raman and Diode-laser-excited Raman. Figure 9 shows spectra of the epoxy cure system before and after curing performed with FT-Raman spectroscopy.

Figure 9: Raman spectra before during and
after curing of DER332/Jeffamine T-403.
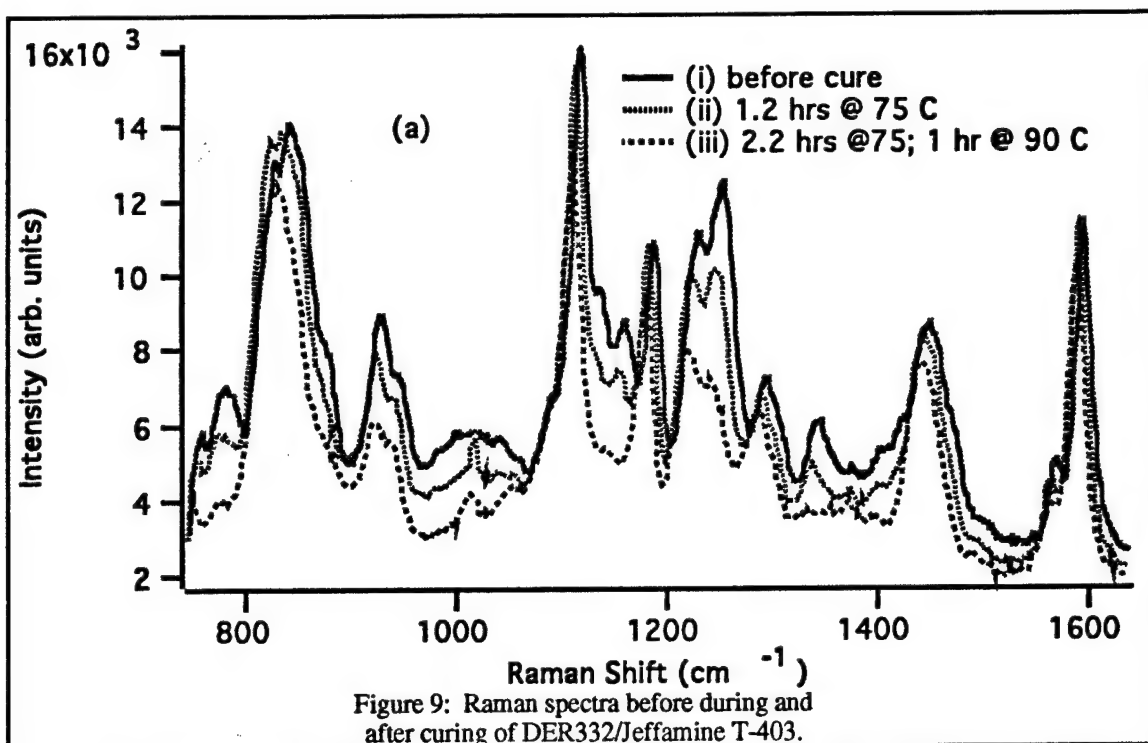
A major concern of one of the students in my group has been the transfer of heat during the curing process in thick-section parts, and the relation of heat transfer to curing kinetics. As a result, we have (with a collaborator in the USC Department of Chemical Engineering, Dr. Eric Markel) made measurements inside 1-inch cylindrical sections of polymer (for ease of comparison between experiment and predictions). Figure 10 shows the experimental setup for a multi-probe experiment in which five separate locations within a cylindrical polymer sample were interrogated. Local temperature at each of the five probe sites was monitored with a thermocouple situated at the fiber probe tips. Excitation for each probe was derived from an Argon ion laser which was beam-split into five beams and directed to the five separate excitation fibers. Returning scattered radiation was detected with a charge coupled device (CCD) array simultaneously using five detection bins, and all spectra were analyzed using principal component analysis.

A sample result from these measure-ments is shown below in Figure 11, in which a set of Raman spectra from four locations (one of the five optical probes failed during the experiment shown in Figure 11) inside the thick polymer are reproduced.

Figure 10

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Spectra such as these are used to determine the per-centage of curing in the polymer (via Principle Component Analysis, PCA) at each location in the sample as a function of time. Reaction rates determined from these measure-ments can be compared to theor-etical reaction rates, with results that are in good agreement.

Theoretical rates are relatively simple to produce for simple geometric shapes of thick polymers.

Figure 11

However, complex shapes and components manufactured with anisotropic elements (e.g., embedded graphite fibers) are substantially more difficult to model and may themselves be irreproducible, since most thick-section composite parts are prepared by hand. An experimental measurement of curing would be highly advantageous in these situations.
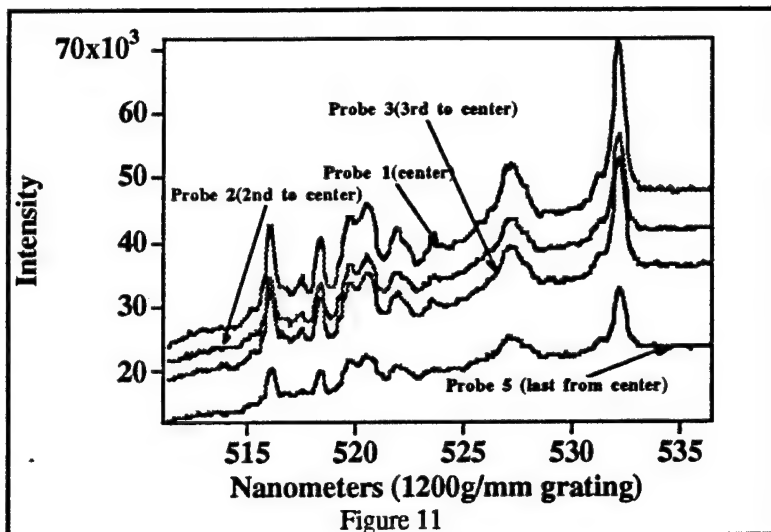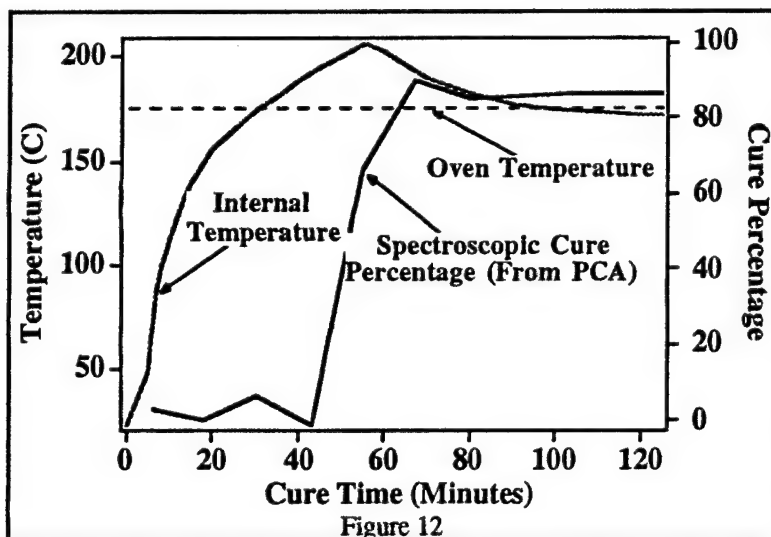
Figure 12

Figure 12 shows the result for a single point in the center of a 1"-thick polymer (the Ciba-Geigy poly-imide). In this case, the oven temper-ature was set at 180 C, and the initial part temperature was 30 C. Following an induction period necessary for heat to begin to transfer to the center of the part, the internal temperature begins to climb. As the rate of polymerization increases (approximately exponen-tially) with temperature, heat is generated internally in the part and the temperature exceeds that of the oven by over 20 C. It is evident from study of Figure 12 that the internal heat which raises the temperature of the polymer center is not due to the curing of the polymer in the center. This is because the reaction of the center only proceeds slowly until the temperature is already elevated above the over temperature. At this point, the reaction proceeds very quickly to completion.

Cursory visual examination of parts prepared in this way show even curing of the exterior of the part, with brittle, deeply colored polymer in the very center which is presumably highly stressed. We believe that complex parts can be examined in this way during curing to control these runaway exotherms in a real-time situation.

EVANESCENT THIN-FILM MEASUREMENTS

The refractive index of the epoxy selected for this study exceeded the refractive indices of typical silica-core optical fibers. Consequently, evanescent spectroscopy of this polymer was not possible with these fibers. Figure 13 shows the refractive index of

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the DER332-Jeffamine T403 polymer as it changes during the curing process. The Ciba-Geigy Polyimide is similar in refractive index, and is strongly colored. In order to perform evanescent Raman, a core material with an index greater than the maximum index attained in the cure is necessary - an index greater than about 1.547 at the sodium D line. The indices of the typical silica fibers we utilized were all near 1.45-1.50 and could not be used. Some measurements were attempted with sapphire rod supports (refractive index > 1.6), but these were experimentally difficult to undertake and it was not clear that a glass-polymer interface could be suitably mimicked in this way.

Change of Refractive Index During the Cure of DGEBA/T-403

Figure 13
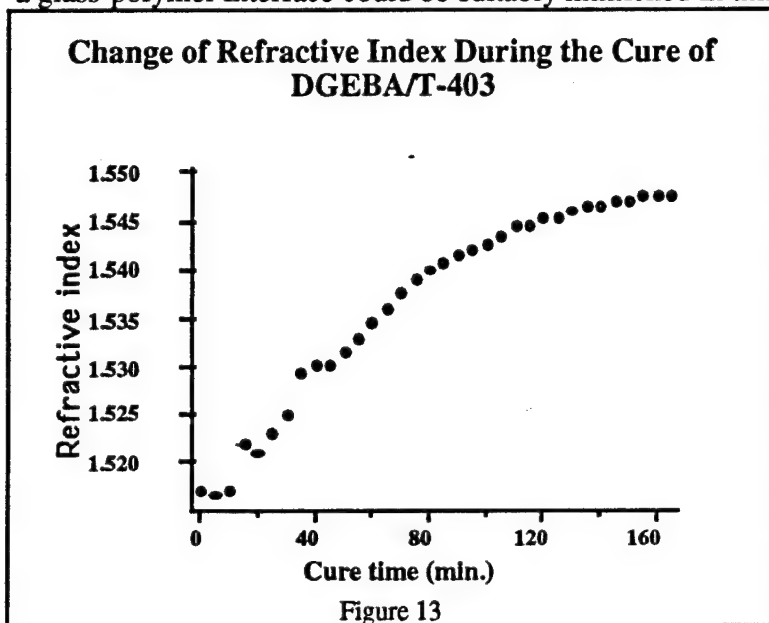
More recently, we have initiated a collaboration with scientists at NIST who are manu-facturing high-index fibers for evanescent NIR spectroscopy. If joint research con-cerns on the NIST partners behalfs can be addressed, we expect to conduct research with these new fibers late in 1995.

NON-EVANESCENT THIN-FILM MEASUREMENTS

We developed a novel method for interrogating variable-thickness thin polymer films and studying them during the curing process. Figure 14 below shows the experimental layout for the technique.

At the left of Figure 14, an optical fiber enters a vial containing the uncured liquid polymer. The fiber is driven by an ultramicrometer for positioning accuracy near 10 nanometers. The fiber is driven by the micrometer through the liquid polymer until it contacts a flat plate, and is then withdrawn to a specified position relative to the plate to interrogate the thin polymer film compressed between the fiber and plate. Laser excitation directed down the fiber excites only the polymer directly in front of the fiber. Scattered light is collected at 90 degrees into a spectrograph.

Top View of Sample Cell

A: Fiber encased in needle   D: F4 lens
B: Sample Cell   E: Entrance slit
C: F2 lens

Figure 14

In an actual experiment, both the fiber and plate are micrometer-driven to ensure that the sample excited is directly in the focal plane of the spectrograph.

The sample thickness can be inferred from the withdrawal of the fiber (and the spacing produced between the fiber and plate thereby), or from the relative intensity of

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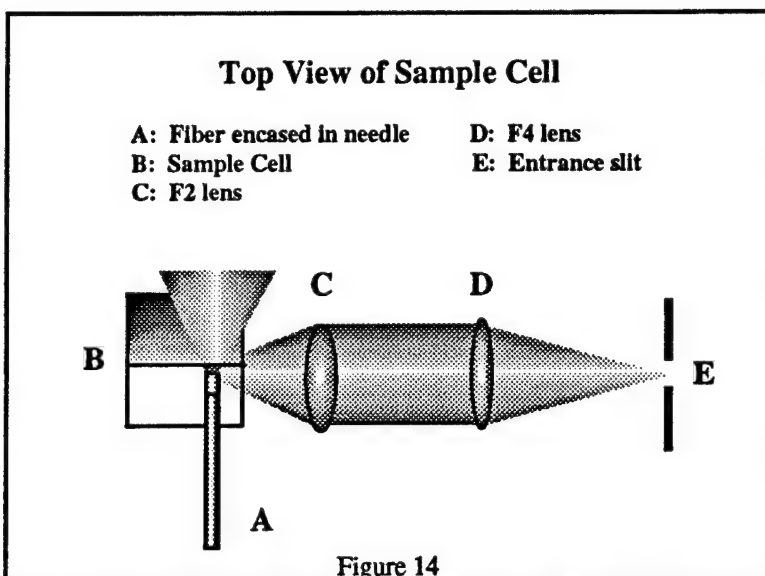
the Raman spectra arising from the sample. This latter estimation is based upon the magnification of the optics in the optical train, the effective width of the spectrograph slits, and the magnitude of the thin-film spectrum to the bulk measurement made by withdrawing the fiber and plate from the view of the spectrograph. (Consider, for example, that if the fiber and plate were in intimate contact -- zero sample thickness -- no spectrum of the sample would be produced at all). The advantages of this experimental setup are that variable sample thicknesses can be easily studied, and the plate can have any type of metallization or coating desired so that numerous interfaces can be studied.

Figure 15 shows an example of the polymer spectrum in bulk (the larger spectrum) and thin-film conditions.

Thin film fiber optic Spectra of DGEBA/T-403

Figure 15
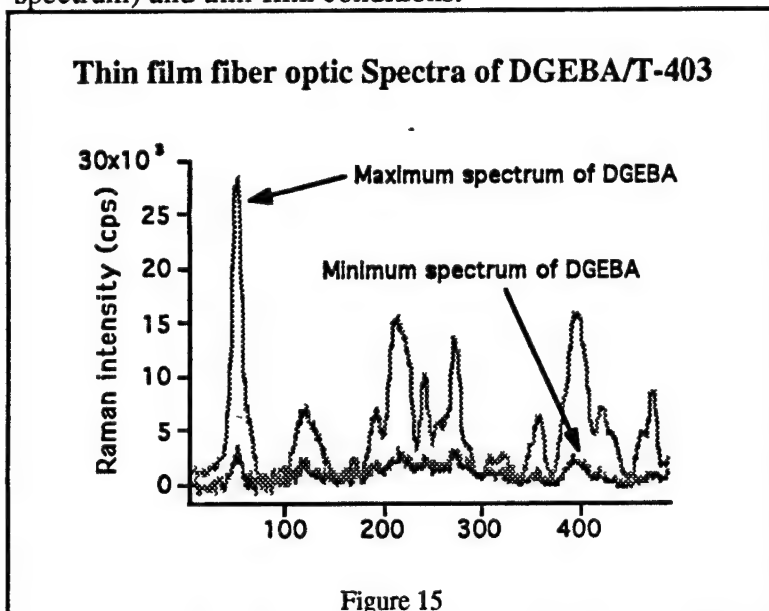
The thin-film (minimum) spectrum shown here corres-ponds to a sample thickness of approx-imately 2 micro-meters. Using con-ventional peak-height or integrated peak intensity cal-culations, the signal-to-noise ratio of the weaker spectrum is near the minimum necessary for useful results. With no additional processing, a 2-μm-thick film is the effective minimum film thickness that can be studied using this method. Figure 16 shows results for the integrated band intensity of a cure-sensitive peak normalized to a cure-insensitive peak.

DGEBA/T-403 Cure Data
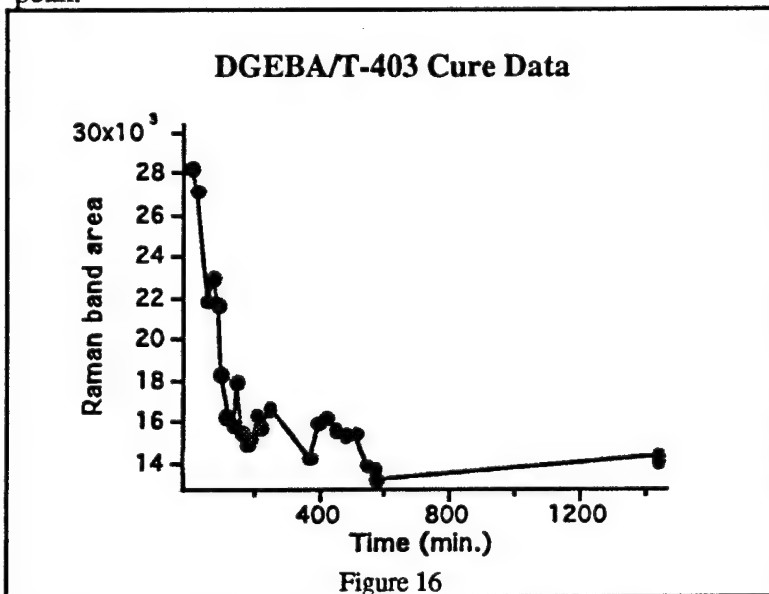
Figure 16

The noise in Figure 16 suggests the data are for a film at our effective minimum detection limit. In order to extend this method to sub-micrometer film thicknesses, multivariate statis-tical processing of the data can be used. Principal Component Analysis (PCA) is a form of pattern-recognition processing (see section on statistical analysis below) that permits improved signal-to-noise in spectroscopic measurements. Figure 17 shows the results of PCA cure analysis for the 2-micrometer-thick film of Figures 15 and 16.

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In Figure 17, the x-axis is time in minutes at room temperature, while the y-axis is a linear combination of spectral wavelengths in the Raman spectrum. These measurments are made at room temperature, and the curing of the polymer at room temperature is a slow process ending at about 75% cure when the glass transition temperature of the partially cured liquid exceeds room temperature and all reaction halts. As the figure shows, this occurs in the thin film at approximately 600 minutes into the cure. The signal-to-noise increase in data interpreted via Principal Component Analysis is substantial, permitting weaker signals to be distinguished from background, and extending the detection limits of this technique to films as thin as 100-200 nm. Work is currently still in progress on comparing these interfacial curing data with bulk curing data.
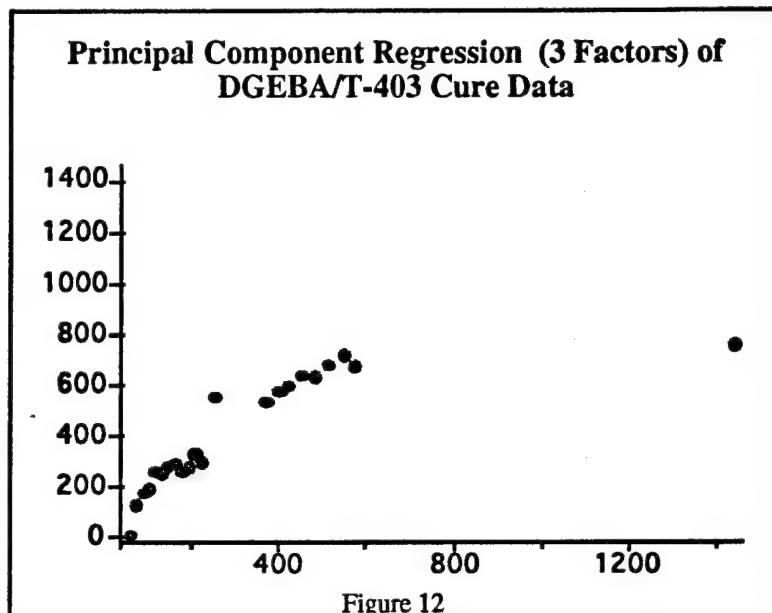
Principal Component Regression (3 Factors) of DGEBA/T-403 Cure Data

Figure 12

Principal Component Analysis

The application of chemometric methods to spectra obtained by fiber-optic Raman spectroscopy addresses the interpretation of optical spectra to determine physical and chemical properties of the polymer.

Raman spectra obtained by fiber optic monitoring during the curing process represent mixtures of several components. Spectral subtraction or least squares fitting of reference spectra is not adequate to resolve mixture spectra when dealing with such "real" mixture problems. Unpredictable chemical changes in polymeric structure complicate spectral interpretation, and reference spectra of pure components are not usually available.

Instead of concentrating on individual features, principal component analysis (PCA) explores relationships between samples and derives a subset of linear combinations of the features that describe the largest proportion of variability.

Accounting for the variability in a data set requires a number of principal components (PC's) equal to the smaller of the number of features or the number of objects in the data set. PCA attempts to represent the higher dimensional data with a smaller set of features, or principal components (PC's). The first PC is the line that best fits the data, with the sum of squares of deviations of the data points from this linear combination of the original axes a minimum. The second and higher PC's are perpendicular to this axis and are ranked in decreasing order of correlation with the data. This decomposition of the data matrix is obtained by eigenvalue-eigenvector analysis, an efficient method which is based on the singular value decomposition[16]. The magnitude of the resulting eigenvalues is a measure of the variance explained by each eigenvector or PC. The number of "significant" eigenvalues indicates the number of real factors or components. Additionally, the PC model can be rotated to make the PC's easier to interpret in chemical terms.

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A major purpose of PCA is dimensionality reduction: a plot of the data projected on the plane formed by the first two PC's permits relationships among the clusters of data points to be visualized in two dimensions. More important, however, is the ability to extract chemically meaningful principal components that represent components of the original mixture.

A variety of software packages for chemometric analysis of data have been used during this project. The limitation on any software analysis tool is the maximum matrix size which the program (or computer platform on which it runs) can invert. The first software tool used here was SYSTAT, a UNIX-based statistical programming language. The limitations of SYSTAT prevented analysis of data matrices larger than 60 X 60 arrays of double-precision values.

A software package available from Infometrix, Inc. called Pirouette® was obtained which was capable of inverting substantially larger arrays - larger than 1000 X 60. Subsequently, the MATLAB programming language was added with new computational facilities to allow inversion of data matrices larger than 1000 X 500 arrays of double-precision numbers. For routine statistical exploration of data, Pirouette® proved convenient and powerful. MATLAB programs, however, were more versatile and provided additional tools for visualization.

To illustrate the effect that application of PCA can have on data analysis, consider Figure 18 below.

In this figure, thin-film measure-ments have been made as a function of micro-meter position. In other words, the sample pathlength is varied during this experiment, and the integrated area of an epoxy Raman peak is plotted vs. micro-meter position to help determine the sample thickness. In this case, the optical fiber is advanced toward a wall, squeezing polymer out of the way until contact is made, then the fiber is withdrawn. From these data, sample thickness appear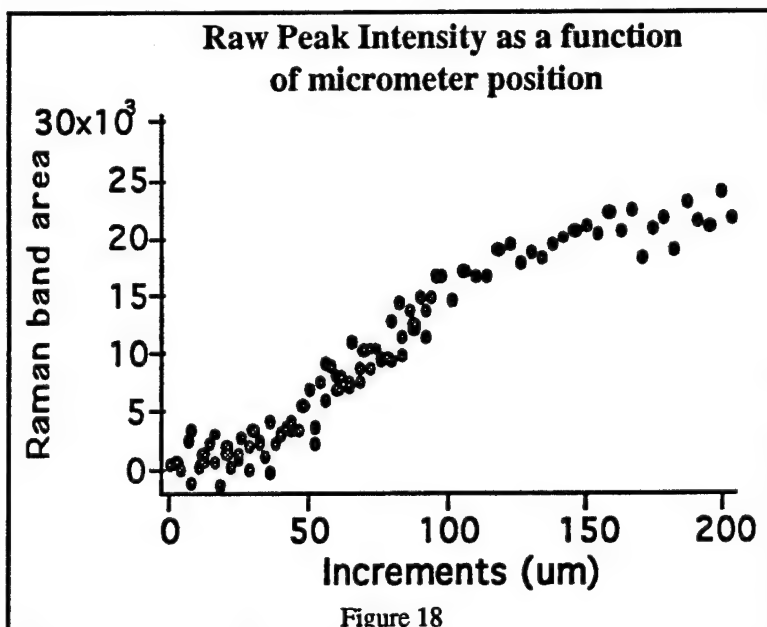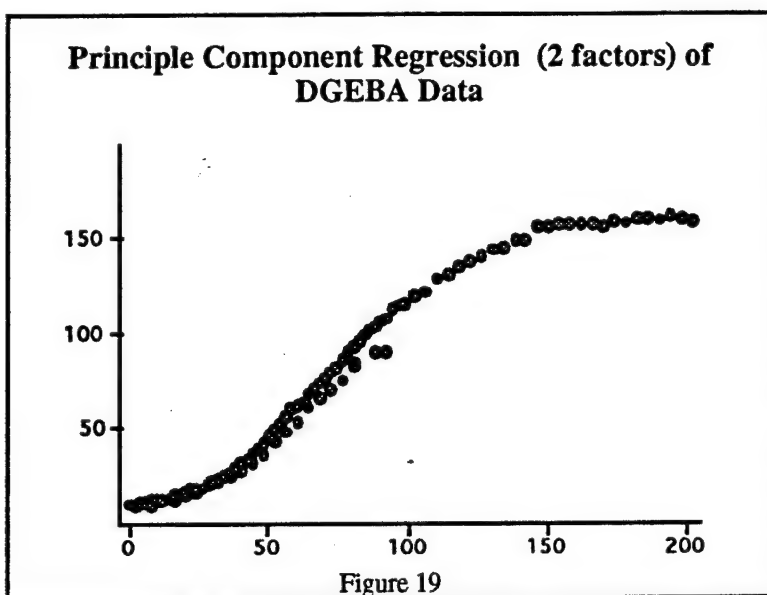s independent of direction (approach or withdrawing). Figure 19 below shows the results of PCA analysis of the same data shown in Figure 18.

Raw Peak Intensity as a function of micrometer position

Figure 18

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Principle Component Regression (2 factors) of DGEBA Data

Figure 19

The substantial improvement in sig-nal-to-noise intro-duced by the multi-variate statistical analysis allows the analyst to view the subtle distinction between data points acquired with the micrometer driven in the forward versus reverse directions, caused by hysteresis of the mechanism.

EPOXY-METAL INTERFACIAL CHEMISTRY VIA SERS

Recently this laboratory has developed a method for producing metal colloidal suspensions in commercial polymers capable of producing surface-enhanced Raman scattering. These suspensions have a variety of uses, one of which is to study the chemistry of molecular adhesion at the metal-polymer interface.

Surface-enhanced Raman scattering (SERS) was discovered in the mid-1970's, and has been the subject of intense study[20]. While normal Raman scattering is a relatively weak phenomenon, adsorption of a molecule at a metal surface can lead to enhancements of the Raman scattering of the molecule by factors approaching 10^5-10^6. This gives a spectroscopic entry to the study of monolayer surface-adsorbed species -- particularly of the chemical bonding present at a metal surface. The drawback of SERS is that only a few metals are known to produce it (Ag, Au, Cu and a few others weakly), and the surfaces must be prepared properly: they should be fresh and rough. Colloidal metal particles produced *in situ* provide such metal surfaces.

The preparation method developed by this laboratory involves preparing a concentrated solution of Ag^+ in Jeffamine T-403, mixing this solution in proportion with DER332, adding solid $NaBH_4$ to reduce the mixture, and curing the resulting brown solution. Ag metal particles precipitate from solution during the curing of the polymer. The exact proportions of T-403 and DER332 along with the rate of heating appear to determine the size distributions of the Ag particles, with aggregate sizes <0.5 μm. The resulting polymer is brown and cloudy in color, but exhibits less fluorescence than a clear, unreduced sample of the same polymer because of the fluorescence-quenching effects of the metal in suspension.

Figure 20 shows the Raman spectrum of the DER332/T-403 polymer with the precipitated Ag colloid. The spectrum of this material changed upon intense illumination with a laser -- new features already present in this material (but not normally present in the clear polymer) increased in magnitude. Figure 20 shows the spectrum prior to intense illumination, along with the spectrum of the differences caused by laser annealing. The difference spectrum nearly recovers a spectrum of a new species produced by the laser heating. Further SERS work in this laboratory has shown that the same new spectrum is obtained by post-curing of the polymer in a normal curing oven. The new peaks are, however, present in the spectrum even before additional heating is provided -- they merely increase in magnitude with heating. A slight shifting of the vibrational frequencies is also observed with additional heating.
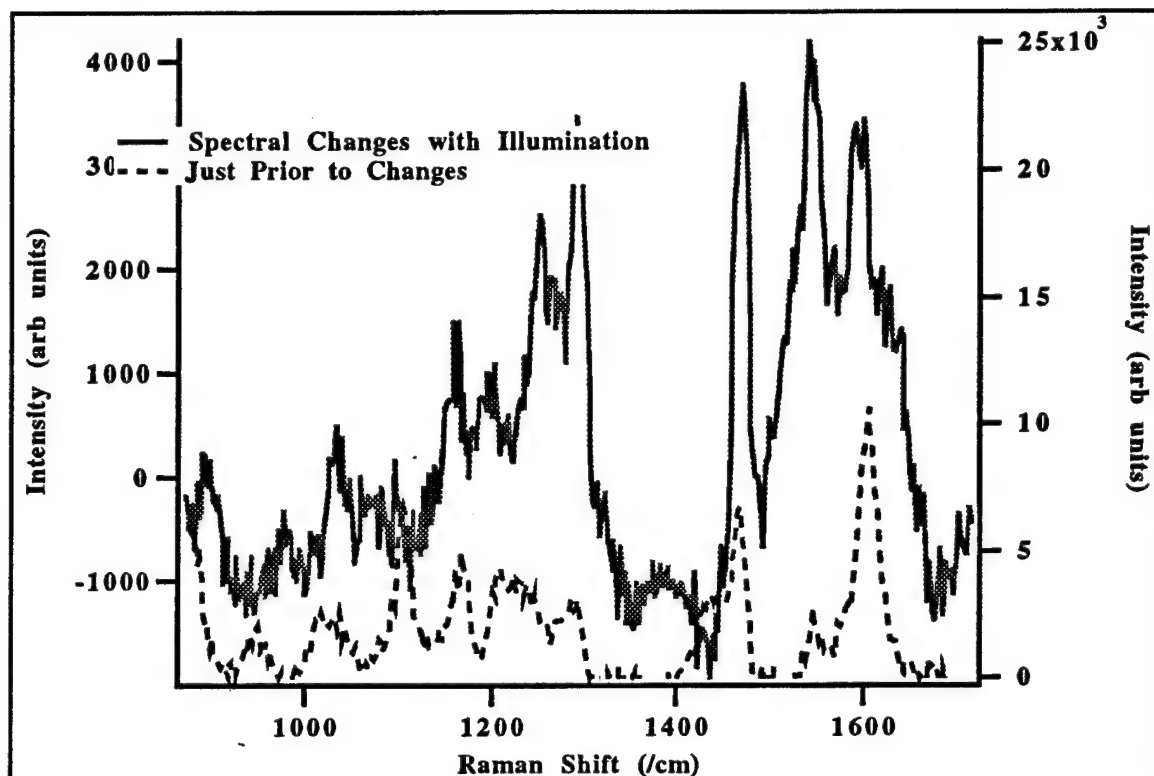
Figure 20: (dashed line) spectrum of the DER332/T-403 polymer prior to laser annealing. New peaks appear in the spectrum even prior to annealing. (solid line) difference spectrum showing approximate spectrum of "new" species observed upon annealing -- actually increased intensity of the new peaks seen before annealing.

The origin of the new features observed in the spectrum upon introduction of the Ag colloid apparently lies in surface-adsorbed DER332 which has not reacted to form part of the polymer. Figure 21 shows the same difference spectrum in Figure 20 plotted on a scale with the SERS of monomer DER332 obtained from a standard water-based colloid. These are essentially identical, given that the difference spectrum is complicated by subtle differences in fluorescence of the polymer and other heating effects.

The nature of the bonding between the DER332 and the metal surface can be deduced from the SERS spectrum. The orientation of the DER332 units on a metal surface is apparently the same whether the DER332 is in a dilute aqueous solution (we were able to observe <200 ppb DER332 in water using SERS) or at a high concentration in a polymer. The surface-enhanced effect is normally greatest for vibrational modes of the molecules which are vibrating perpendicular to the metal surface. In the case of DER332 at the metal surface, some sort of attachment to the metal is indicated by the large shifts of vibrational energies; the enhancement of out-of-plane vibrational modes rather than the in-plane vibrations of the phenyl rings seems to indicate the molecule adsorbs to the surface via a π-bonding interaction of the aromatic electron clouds of the phenyl rings. Hence, the molecule appears to "lie flat" on the metal surface, held in place by an electrophilic attraction of the metal surface for the electrons in the π system of the DER332.
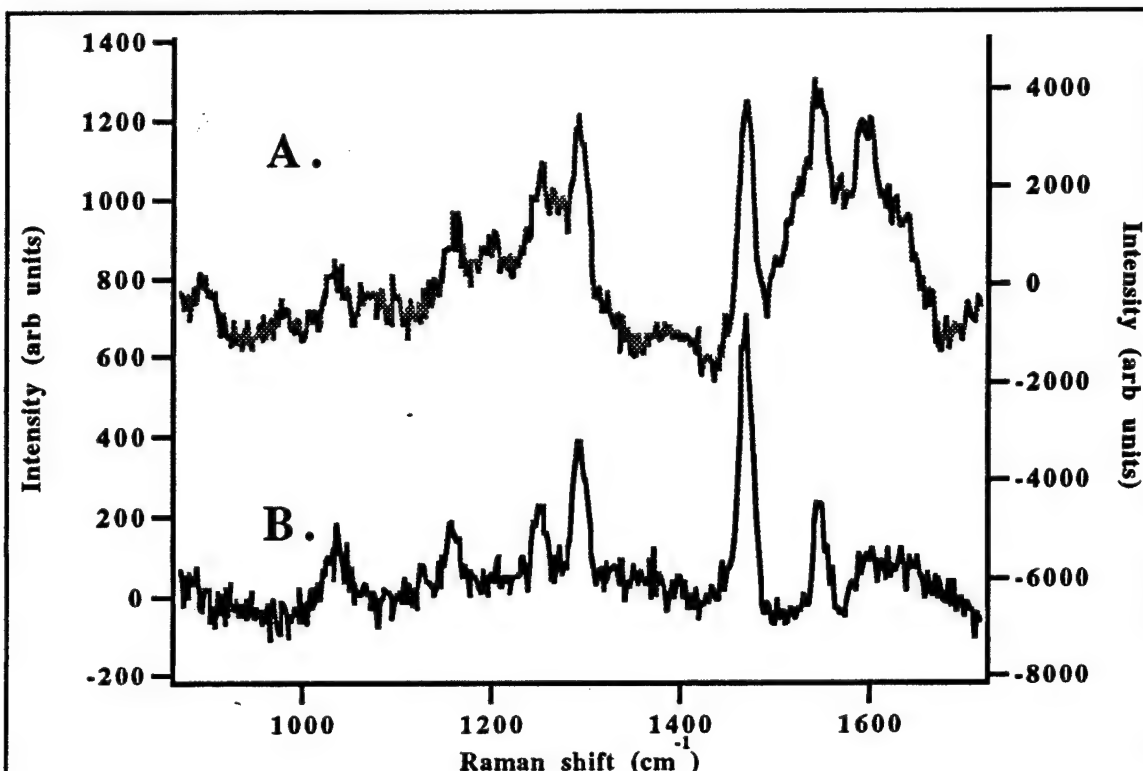
Figure 21: (A) difference spectrum shown in Figure 20. (B) SERS spectrum of 200 ppb DER332 monomer in aqueous solution using an aqueous Ag colloidal suspension.

Electrode-based SERS measurements produce identical SER spectra to those observed in the polymer when DER332 is used as the analyte. The use of electrodes allows the potential of the surface to be controlled precisely, and this work has shown that a very negatively-biased surface is necessary for DER adsorption. In the case of the polymers and hydrosols above, negatively-charged surfaces were obtained by the addition of chemical reducing agents (e.g., $NaBH_4$).

A curious observation regarding these materials can be made: no evidence for SERS of polymerized DER332 can be found, despite the fact that the electronic structure of the π system of the DER332 remains intact upon polymerization. This observation has one important result and at least two possible causes. First, the result is that the chemical bond between the polymer and a metal surface is extremely weak. Secondly, the causes may be: (a) loss of the epoxide groups upon polymerization, which may help direct the bonding of the DER332 to the metal, and (b) replacement of the small epoxides with Jeffamine T-403 groups which are bulky and may prevent the DER332 from assuming a bonding configuration with the surface.

A NOVEL FIBER-OPTIC PROBE FOR IN-SITU MONITORING

A novel probe design for in-situ fiber-optic Raman spectroscopy has been tested and employed for real time monitoring of polymer curing in both thin film and bulk measurements. Multivariate analysis was employed to interpret and analyze the numerous spectra taken during analyses. Multivariate techniques show that both curing and sample internal temperature information can be derived from the Raman spectra.

In polymer analysis, the strength of a processed composite depends to a great extent on the chemical properties of the polymer matrix. Laboratory analyses are often performed with differential scanning calorimetry (DSC), because the curing of these polymers can be controlled in a pseudo-isothermal environment. The sample in these
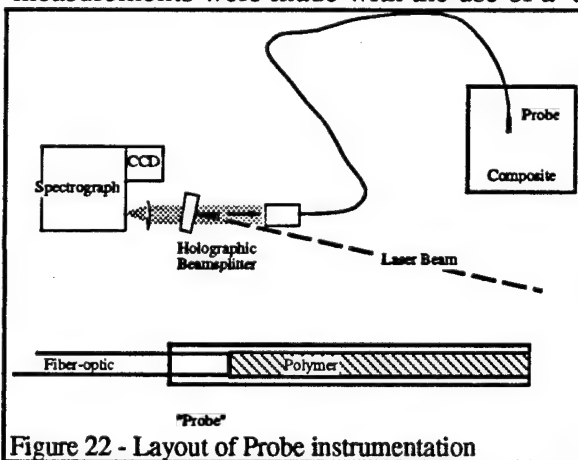
21

measurements is small and thin enough that internally generated heat from exothermic polymerization is efficiently conducted from the sample. However, in industry, most polymers and composite parts are thick enough that internal heat generated by curing is not removed quickly. This makes DSC less than ideal for bulk polymer analysis. Poor thermal conductivity coupled with internal heat generation from a cure reaction can cause temperature and reaction gradients, runaway exotherms (îhot spotsî), and residual thermal stresses--all of which can lead to internal damage, poor bonding between matrix and fibers, and premature structural failure.

Raman spectroscopy for in-situ analysis of polymeric compounds has become more popular and successful with the advent of lasers, holographic filter technology, charge coupled devices, and fiber-optics.[21-8] Raman scattering can be acquired from samples at fairly large distances (e.g. >100 meters) via fiber-optics,[29-31] and this has made remote analysis more practical.

Fiber-optic Raman has the capability to directly monitor curing reactions in both bulk and thin films. Raman is inherently weak. In our studies we propose a new type of fiber-optic in-situ probe that enhances signal-to-noise such that it is possible to have direct monitoring of cure chemistry in real time. These probes permit rapid data acquisition of spectra with large signal-to-noise ratios, from which temperature and chemical structure can be determined. Multivariate techniques can be used to intrepret these Raman spectra quickly and quantitatively.

Reagents. A tripolyoxypropylenetriamine-encapped diglycidylether of bisphenol-A (DGEBA) epoxide was prepared by reacting DGEBA (99%, Dow Chemical DER 332, epoxide equivalent weight 173.0g/eq) polyoxypropylenetriamine (99%, Texaco Chemical Jeffamine T-403, amine hydrogen equivalent weight 50.9 g/eq) in a 100:45 w/w ratio. The mixture was degassed under vacuum and used immediately. The chemical structure, reaction and characterization of the reaction of DGEBA and polyoxypropylenetriamine have been shown previously.[22,32-3]

Apparatus. The instrumental apparatus is shown in Figure 1. The in-situ measurements were made with the use of a one-fiber Raman system employing a new probe design in which the distal end of the fiber is inserted into a Teflon™ tube that has been filled with the epoxy mixture. Excitation was achieved by focusing 30 mW of the 488 nm line of a Coherent Innova 305 argon laser onto the proximal end of the fiber with an f/2 lens. The collected Raman scattering from the distal end was collimated through a 488 nm holographic filter (Kaiser Optical Systems Inc.) to attenuate the excitation line, and then focused onto the slit of a Chromex 250IS imaging spectrograph. The spectra were collected with a thermoelectrically cooled CCD camera (Santa Barbara Instrument Group) cooled with a water jacket to -50 C.[34]

Figure 22 - Layout of Probe instrumentation

The probe was constructed from a 200 µm-core, two meter long silica fiber (Polymicro Inc.) The proximal end was fitted with an ST-connector, while the polyimide buffer was burnt away from the distal end. The distal end was then inserted into the opening of a 200 µm ID Teflon™ tube with a length of 40 mm. The tube end was reamed out with .008" and .009" guitar string to allow the fiber to fit properly. Epoxy mixture was then injected into the tube until it was filled.

Thermal analyses were performed on a Perkin-Elmer DSC7 differential scanning calorimeter. All samples were placed in standard aluminum pans and subjected to a temperature range of 50-250 C at a scan rate of 10 C/min.

The thin film measurements were performed by heating the epoxy mixture filled tube in a stirred oil bath. With such a small volume (1.5 mL) of polymer and large surface area, a negligible amount of heat is trapped in the sample itself during the curing, giving it a temperature and reaction rate characteristic of the material surrounding it. Bulk measurements were made by taking an identical tube and placing it into an 8 dram vial filled with 25 mL of the same epoxy mixture. In these measurements the heat generated by the epoxy mixture surrounding the tube causes the internal temperature of the sample inside the tube to exceed the oil bath temperature, reaching temperatures in excess of 180 C. Both tube and vial were placed into the oil bath. The temperature of the oil was monitored with a thermocouple.

Sample Runs. Three types of experiments were performed: Thin film curing, bulk curing, and cure-independent temperature shift studies. All experiments were done with the aforementioned instrumental set-up. All spectra were acquired in 30 second exposures using 30 mW of laser power. A 1200g/mm grating blazed at 750 nm was employed for all runs and was centered at 572 nm (3000 cm^{-1}). The slit width changed for each experiment and was used as the means to restrict the amount of signal reaching the CCD so as not to overload it with too much signal, with changing slit widths from 25 to 10 μm being the best method for controlling spectral intensity. This was determined by the maximum size the slit could be without overloading the detector in a 30 second exposure. Thirty second exposures were performed because the epoxide cure is relatively slow hence the need for thousands of spectra acquired during a four hour cure cycle was unnecessary. The system has the capacity to monitor the curing with exposures far less than one second.

The dramatic increase in signal for the tube system is attributed to the waveguiding property of the tube. The tube has a lower refractive index than the epoxy mixture, thus causing the laser radiation to be waveguided down the length of the tube. The subsequent Raman scattering induced is waveguided back to the fiber, and ultimately to the detector causing a 15X increase in collected Raman intensity.

The "thin film" (1.5 mL) tube samples were cured at 90 C for four hours. At that point the temperature was increased to 150 C, and held constant for 30 minutes. Isothermal analysis from DSC predicted 90% cure after 4 hours at 90 C and 99% cure after 30 minutes at 150 C. The bulk measurements were cured for 4 hours at 90 C. The amount of heat generated by the curing of the bulk polymer (25 mL) was enough to increase the rate and percentage of cure that no increased temperature curing was needed.

Previous studies have focused on the fingerprint region for following the sample curing chemistry.[21-3,28] It is also known that the C-H stretching region has cure sensitive peaks, and the monitoring of the curing reaction can be performed in this region as well as the fingerprint.

Figure 2 shows Raman spectra taken before and after curing. The peak at 3007 cm^{-1} disappears after curing and there appears to be a shift in the peak at 3069 cm^{-1}.

Heat flow between the bulk polymer and the polymer in the tube is rapid on this scale. This was determined by filling a tube with cyclohexanol (m.p. 20-22 C) and placing it into a 0 C ice bath. The tube was removed and left to stand in air at 21 C. The cyclohexanol completed its melt in less than one minute.

The cure-independent temperature shift experiment was performed in response to the observation that peaks shifted when the temperature was raised to 150 C in the thin film experiments. A thin film sample was cured for 30 minutes at 150 C, allowed to cool to 51 C, and then reheated to 150 C. Spectra were taken continuously during the curing, cooling and heating processes.

Figure 23 - C-H region spectra before and after curing

Data Analysis. Variability in a spectral data set caused by sample curing, temperature changes, and instrument response are best handled by multivariate analysis. Normalization and baseline subtraction of spectra were employed so that large groups of spectra could be compared and correlated to one another, so that any variance seen is due to effects of the sample--not the instrument. The remaining variability can be analyzed by principal component analysis (PCA). PCA is a coordinate transformation which attempts to express the variability of a data set in the fewest possible dimensions. Accounting for all the spectral variability requires a number of principal components (PCs) equal to the smaller of the number of variables or the number of samples.[35-6] However, as with the data described here, data can often be accurately represented by a small subset of the most significant PCs, e.g. the PCs that describe the largest portion of the data.

Multivariate analysis was performed with the use of a software package Matlab (The Math Works Inc, Natick, MA). Every second spectrum for each thin film and bulk measurement was converted to ASCII, imported, and analyzed. All spectra taken in the temperature shift experiment were converted to ASCII and analyzed. All spectra were baseline subtracted by implementing a cubic spline fit that models fluorescence background, and normalized to unit area prior to principal component analysis. This isolates stoichiometry changes from instrumental and sampling efficiency changes in each spectrum.[37] For a first order curing reaction, a bivariate plot of the two most significant components should yield a straight line. These plots were used to uncover the existence of spectral changes unassociated with epoxy curing. Additionally, the spectra were also mean-centered, which is subtraction of the average spectrum prior to principal component analysis. In this case, only one principal component is significant for an ideal first order reaction. Plots of this PC vs. time are hence used to track the progression of the epoxy cure.

Dependence of Signal on Tube Length. A measurement of Raman intensity vs. sample tube length was performed. The intensity was measured from the peak at 3069 cm^{-1} with the baseline subtracted. The tube performs poorly as a waveguide and no appreciable gain in intensity could be achieved with a tube longer than 40 mm. The effective decay-length of the enhancement was aproximately 12 mm. Short sections of tube greatly enhance the collection efficiency, which is ideal for in-situ
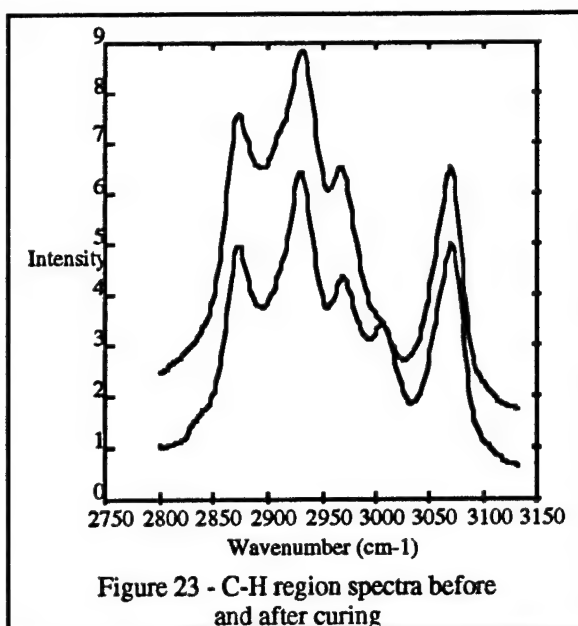
24

analysis/monitoring since smaller probes will reduce the chance of compromising the structural integrity of a large polymer section or composite. As a comparison, the distal end of the probe with no tube was placed into a one dram vial filled with epoxy mixture and the relative intensity of the 3069 cm-1 peak was 5500. A tube length of 25 mm gives an order of magnitude increase in signal.

Effects of the Tube on the Curing Process. In previous in-situ studies with fiber optic probes and epoxy curing, we often saw cracks propogating from the fibers, but the tube-probe samples did not show this behavior. This was probably due to the Teflon™ tube's ability to "give" and relieve stress in the polymer. Probes that consist of glass fibers alone or fibers encased in a rigid material cannot perform in this manner.

Multivariate Analysis. For the multivariate analysis work, the C-H spectral region has been broken down into three areas: the area inclusive of the 3069 cm^{-1} peak, the four adjacent peaks with Raman shifts of (3007, 2971, 2931, and 2873 cm^{-1}), and all five peaks together. This is done because the 3069 cm-1 peak is effectively cure-insensitive, while the others appear to change substantially during the cure. Figure 24 shows a plot of PC2 vs. PC1 analyzing all five peaks together. As stated in the experimental, a bivariate plot of this type for a first order reaction should yield a straight line. Both the thin film and bulk measurements yield straight lines. Although there are also temperature related spectral changes, these are very small compared to the cure related spectral changes and, hence, are not observable in this plot. Figure 25 shows a plot of PC1 score vs. curing time. The plot shows that the bulk samples cure faster than the thin film samples. This is expected because of the internal heat generated by the exothermic cure of the bulk epoxy increases the rate of the curing reaction. This shows that the tube probe is an effective method for monitoring both thin films and bulk samples.
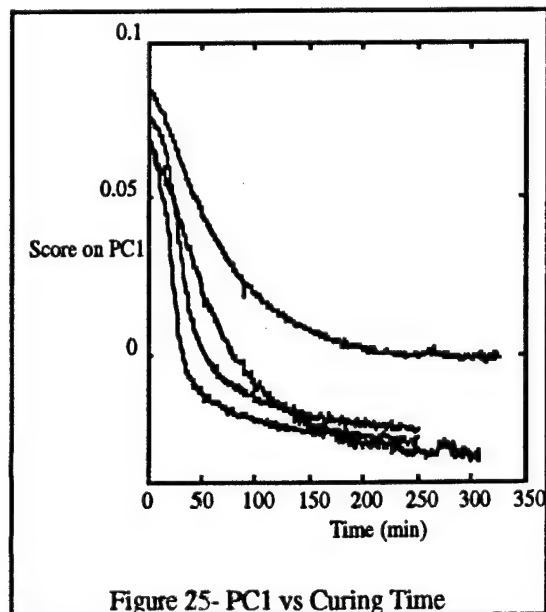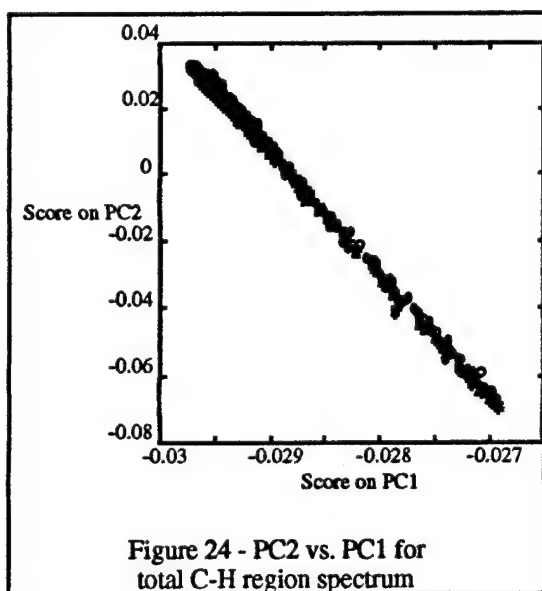

Figure 24 - PC2 vs. PC1 for total C-H region spectrum
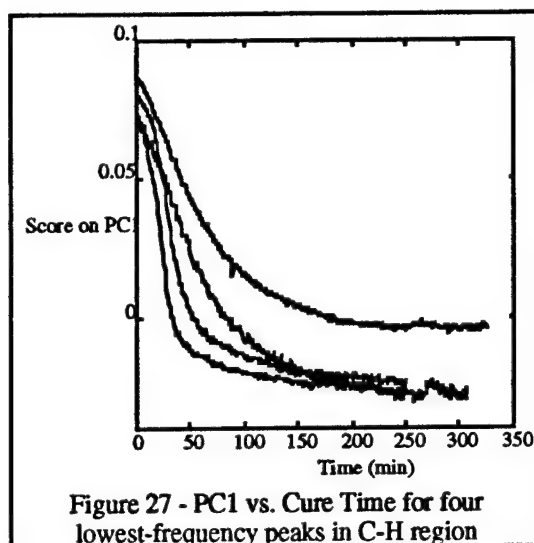
Figure 25- PC1 vs Curing Time

Figure 26 shows a plot of PC1 score vs. curing time for the thin films and bulk samples using only the 3069 cm^{-1} peak. After 240 minutes, the temperature was increased from 90 C to 150 C for the thin film samples. This cure-insensitive peak changes only slightly during the cure, but shows a significant change after the temperature is ramped. Figure 27 shows the same plot, but of the four cure-sensitive peaks between 3007 and 2873 cm^{-1}.

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Figure 26 - PC1 vs. curing time
usng only the 3069 cm⁻¹ peak

Figure 27 - PC1 vs. Cure Time for four
lowest-frequency peaks in C-H region
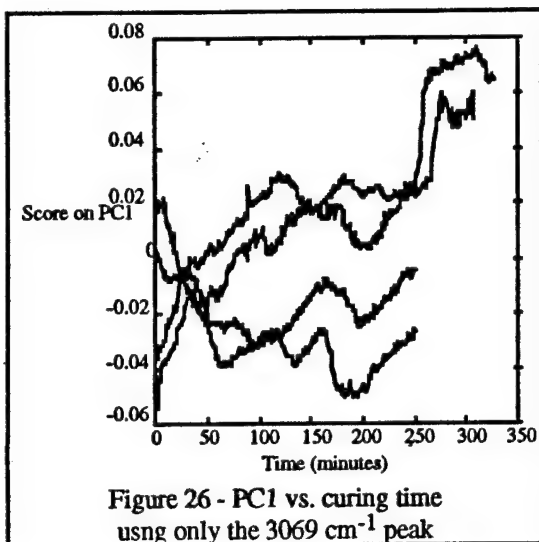
The plot looks identical to that obtained using all of the peaks and seems to contain curing information only. Evidence that the four peaks between 3007 and 2873 cm⁻¹ contain mostly curing information is shown in Figure 28. This is a plot of PC2 vs. PC1 obtained using the four peaks between 3007 and 2873 cm⁻¹, and it shows a pattern much like that of Figure 24. Figure 29 is a plot of PC2 vs. PC1 for the cure-insensitive 3069 cm⁻¹ peak alone. There is very little change during the curing cycle, but a change occurs after the temperature has been elevated to 150 C.

Temperature-Dependence of Stokes Raman. In the temperature shift experiment, the temperature of the sample was initially 150 C, where it was allowed to cure.

Figure 28 - PC2 vs. PC1 for four
lowest-frequency peaks in the C-H region

Figure 29 - PC2 vs. PC1 for the
cure-insensitive peak at 3069 cm⁻¹
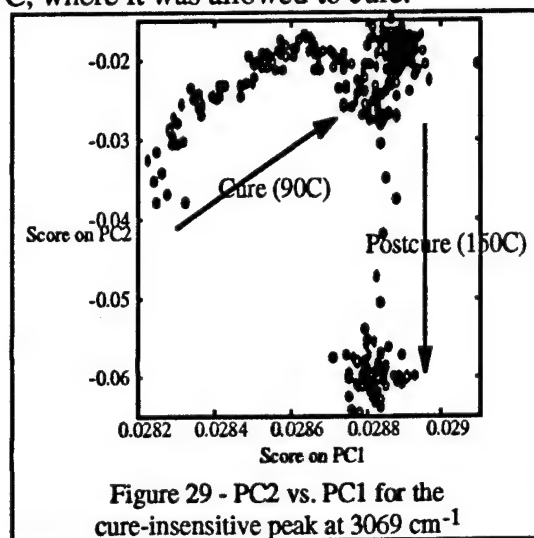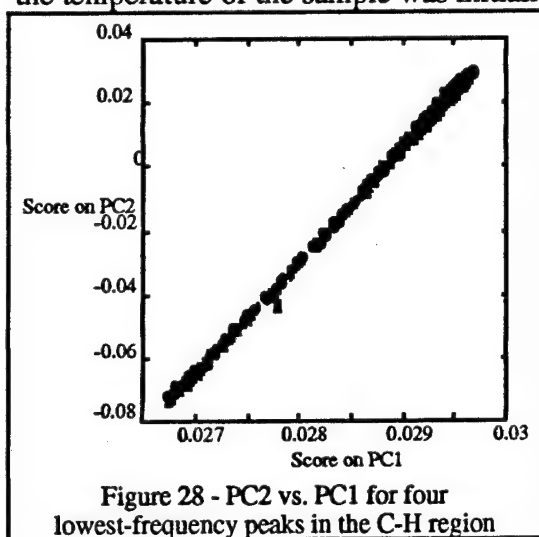
The sample was then gradually cooled to 51 C, and then re-heated to 150 C. Figure 30 shows a plot of PC1 score vs. time. The sample was held at 150 C for 32 minutes, cooled over 57 minutes to 51 C, and then re-heated to 150 C in 24 minutes.
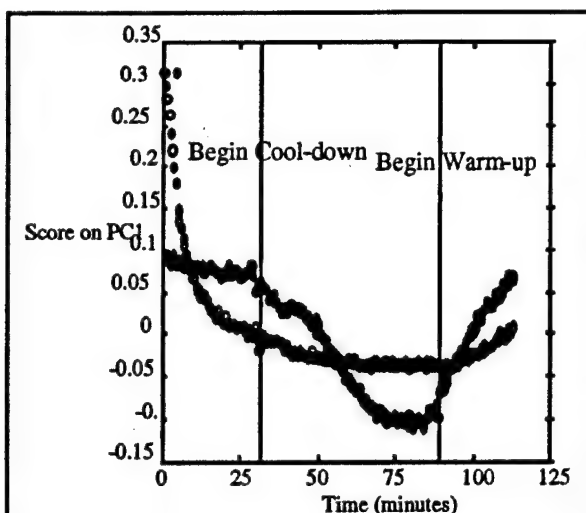
Figure 30 - PC1 Score vs. time for cure-sensitive (open circles) and temperature-sensitive (filled circles) portions of the C-H vibrational region.

The filled circles are the plot for the PC1 score for the 3069 cm^{-1} peak alone and the open circles are the plot of PC1 score of the four peaks between 3007 and 2873 cm^{-1}. The 3069 cm^{-1} peak undergoes little change throughout the curing cycle of the epoxide, and changes mostly with temperature. The other four peaks change predominantly during the curing cycle and vary little throughout the warming and cooling of the sample. Further evidence that the 3069 cm^{-1} peak is sensitive predominantly to temperature and that the other four are sensitive to cure is shown in Figures 31 and 32. Figure 31 shows a plot of PC1 score vs. temperature for the 3069 cm^{-1} peak alone. It again shows little variation during the curing cycle, with most change occurring during the heating and cooling of the sample. Figure 32 shows the PC1 score vs. temperature using the four cure-sensitive peaks between 3007 and 2873 cm^{-1}. Most of the variance in this plot occurs during the curing cycle, with little during heating and cooling. It is possible that even after monitoring the curing of a part, the probe can be left in place and used as an optical temperature monitor.

Score plots of the 3069 cm-1 peak and the four peaks between 3007 and 2873 cm^{-1} can be viewed simultaneously as multivariate statistical process control (MSPC) charts to monitor the polymer curing process. When the polymer is curing isothermally, the scores on the MSPC chart for the other four peaks will be decreasing while the scores on the 3069 cm^{-1} peak will be constant. Conversely, during a runaway exotherm, the scores on the 3069 cm^{-1} peak MSPC chart will rapidly increase. During
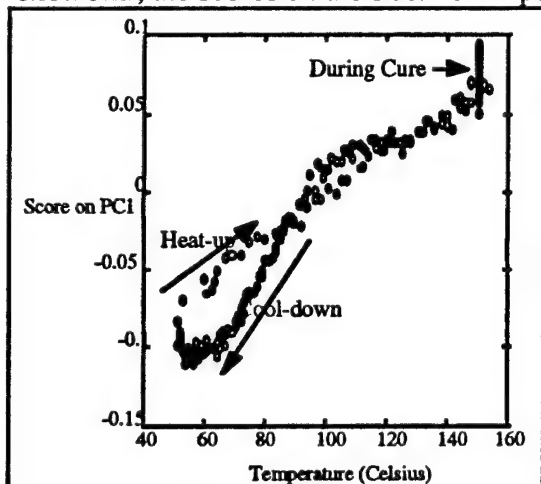

Figure 31 - PC1 Score vs. Temperature for the 3069 cm^{-1} vibration alone
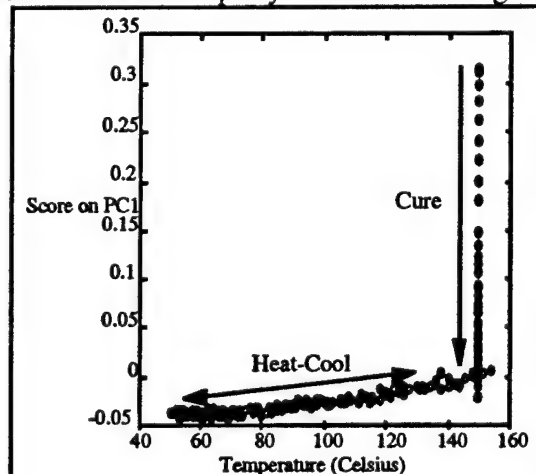

Figure 32 - PC1 Score vs. Temperature for the 4 cure-sensitive peaks

the increased temperature ramping period, the scores on the 3069 cm^{-1} peak MSPC chart will increase sharply compared to the scores on the other four peaks' MSPC chart.

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The Personnel involved in this research over its term have been:

> Dr. M.L. Myrick, PI
> Dr. S.L. Morgan, Co-PI
> Dr. Eric Markel, collaborator, USC-Chemical Engineering
> Chris Calling, Oriel Instruments, Inc. (equipment loans)
> Dr. John Cooper, post-doctoral associate
> Dr. Karl Booksh, NSF Post-Doctoral Fellow
> Katherine Chike, research assistant
> Chris Stellman, research assistant
> James Noll, research assistant
> Jeffrey Aust, research assistant
> Melinda Hale, research assistant
> Wendy Bell, research assistant
> Michael L. McLester, technician

Melinda Hale received a Ph.D. in Analytical Chemistry (S.L. Morgan, advisor) in 1994. She is currently pursuing a second degree in Statistics at USC.

Dr. Cooper is now an Assistant Professor of Chemistry at Old Dominion University, to which he moved in the Summer of 1993.

Dr. Booksh arrived at USC in August 1994, and is currently planning to stay with this research group until his NSF Post-Doctoral Fellowship expires in 1996.

Mr. Stellman and Ms. Bell are currently each in their third year of graduate studies and we anticipate their timely completion of work and graduation in 1996-7.

Mr. Noll and Mr. Aust are each in their fourth year of graduate studies, and we anticipate their completion of work and graduation in 1995-6.

A number of publications and presentations have resulted from this work.

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Fiber-Optic Raman Spectroscopy for Cure Monitoring of Advanced Polymer Composites
Myrick, M.L., Angel, S.M., Lyon, R.E., and Vess, T.M.
Proceedings of the SPE 50th Annual Technical Conference and Exhibits (Detroit, May 4-8, 1992) pp. 2052-2055.

Raman in the Real World
Myrick, M.L., Kolis, J., Parsons, E., Chike, K., Lovelace, M., Scrivens, W., Holliday, R., and Williams, M. presented at Gordon Conference on Analytical Chemistry, Hew Hampton, NH, August 11, 1993.

FT-Raman Studies of a Polyimide Curing Reaction
M.L. Myrick, J.F. Aust, M.K. Higgins, and S.L. Morgan,
presented at Pittsburgh Conference, Atlanta, Ga., March 1993

Raman and Near-IR Studies of the Curing of an Epoxy
M.L. Myrick, K.E. Chike, R. Lyon, S.M. Angel, and T. Vess, presented at Pittsburgh Conference, Atlanta, Ga., March 1993

Factor Analysis of Fiber-Optic Raman Spectroscopy Data From Thermoset Polymers During the Curing Process
M.K. Higgins, J.F. Aust, S.L. Morgan and M.L. Myrick, presented at Pittsburgh Conference, Atlanta, Ga., March 1993.

Remote Cure Monitoring of Polymeric Resins by Laser Raman Spectroscopy
K.C. Hong, T.M. Vess, R.E. Lyon, K.E. Chike, J.F.Aust, and M.L. Myrick
Proc. 38th Intern. SAMPE Symp. (Anaheim, CA, May 10-13, 1993), in press.

Reduction of Dimensionality Concepts for Spectroscopic and Chromatographic Data
S.L. Morgan, M. Higgins, J.F. Aust and M.L. Myrick
presented at Pittsburgh Conference, Chicago, Ill, March 1994.

Pyrolysis GC/MS of a Polyimide as a Function of Curing Time
R. Gallipo, S.L. Morgan, M. Higgins, J.F. Aust, and M.L. Myrick
presented at Pittsburgh Conference, Chicago, Ill, March 1994.

A New Fiber-Optic-Interfaced Micro-Raman Spectrometer
C. Stellman, M.L. Myrick
presented at Pittsburgh Conference, Chicago, Ill, March 1994.

Variable-pathlength Cell for Thin-Film Raman Spectroscopy
K.E. Chike, M.L. Myrick
presented at Pittsburgh Conference, Chicago, Ill, March 1994.

Comparison of thin-film and evanescent Raman Spectra for an Epoxy Curing Reaction
K.E. Chike, M.L. Myrick
presented at Pittsburgh Conference, Chicago, Ill, March 1994.

Development of a Novel Micro-Raman Spectroscope
C. Stellman, M.L. Myrick

presented at Pittsburgh Conference, Chicago, Ill, March 1994.

New Concepts in Polymer Processing
Richard Lyon
presented at the 1994 Polymers Gordon Conference, New Hampshire. July 1994.

Analysis of Raman Spectra in the Curing of Polyimides
J.F. Aust, M.L. Myrick, S.L. Morgan, M. Higgins, D.D. Archibald
presented at Pittsburgh Conference, Chicago, Ill, March 1994.

SERS Using an Ag Colloid in a Commercial Polymer: Interfacial Chemistry
J. Wu, M.L. Myrick
resented at the Pittsburgh Conference, New Orleans, LA, March 1995.

A Study of Polymer Curing by Chemometric Analysis of Data from Raman Spectroscopy
and Pyrolysis GC-MS
R.C. Galipo, J.F. Aust, M.L. Myrick, M.K. Higgins and S.L. Morgan
Federation of Analytical Chemistry and Spectroscopy Societies,
St. Louis, MO, Oct 7-12, 1994.

Fiber-Optic FT-Raman Analysis of a Polyimide Curing Reaction
J.F. Aust, E.J. Markel, and M.L. Myrick
Federation of Analytical Chemistry and Spectroscopy Societies,
St. Louis, MO, Oct 7-12, 1994.

Micro-Raman Spectroscopy of Polymers at the Bulk Interface
C.M. Stellman and M.L. Myrick
Federation of Analytical Chemistry and Spectroscopy Societies,
St. Louis, MO, Oct 7-12, 1994.

Alignment of Mode-Hopped Raman Spectra
K.S. Booksh, C.M. Stellman and M.L. Myrick
Federation of Analytical Chemistry and Spectroscopy Societies,
St. Louis, MO, Oct 7-12, 1994.

Raman Studies of the Curing of Thick Section Polymers
J.F. Aust, K.S. Booksh, E.J. Markel and M.L. Myrick
presented at Pittsburgh Conference , New Orleans, LA, March 5-10, 1995.

Micro-Raman Imaging of an Epoxy at an Interfacial Region
C.M. Stellman, K.S. Booksh, and M.L. Myrick
presented at Pittsburgh Conference , New Orleans, LA, March 5-10, 1995.

A Novel In-Situ Probe for Analysis of Polymer Curing
J.F. Aust, K.S. Booksh and M.L. Myrick
presented at Gordon Conference on Polymers, Henniker, NH, June 26-30, 1995

Surface-enhanced Raman Scattering Using a Silver Colloid Suspended in a Commercial
Polymer
J. Wu and M.L. Myrick
presented at Gordon Conference on Polymers, Henniker, NH, June 26-30, 1995

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FT-Raman Studies of a Polyimide Curing Reaction
Aust, J., Hale, M., Morgan, S.M., and Myrick, M.L.
Anal. Chim. Acta 293(1994), 119.

Raman Spectroscopy With A Low-Cost Imaging CCD Array
Cooper, J.B., Aust, J., Stellman, C., Chike, K., Myrick, M.L., Schwartz, R., and Longmire, M.
Spectrochim. Acta 50A(1994),567.

In-Situ Fiber-Optic Raman Spectroscopy of Organic Chemistry in A Supercritical Water Reactor
Myrick, M.L., Kolis, J., Parsons, E., Chike, K., Lovelace, M., Scrivens, W., Holliday, R., and Williams, M. J. Raman Spectrosc. 25(1994),59.

Surface-enhanced Raman Scattering Using a Silver Colloid Suspended in a Commercial Polymer
J. Wu and M.L. Myrick
J. Phys. Chem. (submitted, 1995)

Characteristics of GRIN Lenses for Raman Spectroscopy
M.L. Myrick and S.M. Angel
Appl. Opt. (submitted, 1995)

Novel In-Situ Probe for Monitoring Polymer Curing
J.F. Aust, K.S. Booksh, and M.L. Myrick
Appl. Spectrosc. (submitted, 1995)

Normalization Alternatives for Processing of In Situ Optical Spectra
J.F. Aust, K.S. Booksh, W.C. Bell and M.L. Myrick
(manuscript in preparation, 1995)

Highlights of Publications

A) FT-Raman Studies of a Polyimide Curing Reaction
Aust, J., Hale, M., Morgan, S.M., and Myrick, M.L.
Anal. Chim. Acta 293(1994), 119.

This paper provides the statistical basis for determination of cure percentage of a polymer from optical Raman data, including an analysis that describes multiple reactions for the same polymer.

B) Novel In-Situ Probe for Monitoring Polymer Curing
J.F. Aust, K.S. Booksh, and M.L. Myrick
Appl. Spectrosc. (submitted, 1995)

This paper describes a probe that can replace thermocouples for cure monitoring. The new instrumentation (developed in this laboratory) is inexpensive (~ $10 in materials), is pliable so that stress does not build up around the probe and result in structural failure, produces excellent Raman spectra even in composites, and can solve the problems of fluorescence in polyimides, etc. Both temperature and cure data can be obtained, and when the use as a cure monitor is completed the probe can remain in place for future measurements of fatigue, stress and heat damage.

C) Raman Spectroscopy With A Low-Cost Imaging CCD Array
Cooper, J.B., Aust, J., Stellman, C., Chike, K., Myrick, M.L., Schwartz, R., and Longmire, M.
Spectrochim. Acta 50A(1994),567.

This paper describes more instrumentation aimed at reducing the cost of Fiber-Optic Raman equipment. Prior to this publication, CCD array detectors cost $20 K or more and were by far the most expensive element of a Raman system. This was the first paper that described a spectroscopically-useful array for <$5 K. As a direct result of this paper and the work associated with it, this instrumentation is being marketed successfully nationwide. This laboratory alone has three such detectors now, and nearly every research laboratory in Raman spectroscopy across the country has purchased at least one. Numerous manufacturers are rushing to meet the challenge posed to their more-costly instruments posed by the new, more inexpensive instruments.

Highlights of Presentations

Surface-enhanced Raman Scattering Using a Silver Colloid Suspended in a Commercial Polymer
J. Wu and M.L. Myrick
presented at Gordon Conference on Polymers, Henniker, NH, June 26-30, 1995

This presentation described a synthetic method and spectroscopic results for the study of metal-polymer interfaces using Surface-enhanced Raman spectroscopy. The polymer matrix with its permanently-suspended metal colloid also has an irreversible illumination-intensity-dependent SERS and fluorescence behavior which make them potential optical recording media. The bonding between a metal and polymer was described in some detail.